⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　平3-223863

⑤Int. Cl.⁵　識別記号　庁内整理番号　㊸公開　平成3年(1991)10月2日

G 03 F 7/039　5 0 1　7124-2H
7/004　5 0 1　7124-2H
H 01 L 21/027

2104-5F　H 01 L 21/30　3 0 1 R

審査請求　未請求　請求項の数 3　（全9頁）

㊹発明の名称　レジスト材料

㉑特　願　平2-19614

㉒出　願　平2(1990)1月30日

Applicant's priority document

⑫発明者　浦野　文良　埼玉県川越市大字的場1633番地　和光純薬工業株式会社東京研究本部内

⑫発明者　中畑　正明　埼玉県川越市大字的場1633番地　和光純薬工業株式会社東京研究本部内

⑫発明者　藤江　啓利　埼玉県川越市大字的場1633番地　和光純薬工業株式会社東京研究本部内

⑫発明者　大野　桂二　埼玉県川越市大字的場1633番地　和光純薬工業株式会社東京研究本部内

⑪出願人　和光純薬工業株式会社　大阪府大阪市中央区道修町3丁目1番2号

明　細　書

1. 発明の名称

レジスト材料

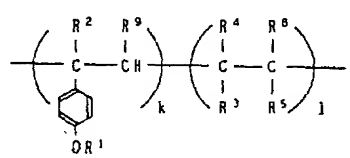
2. 特許請求の範囲

(1)酸雰囲気下で加熱により化学変化を受けてアルカリ可溶性となる官能基を有する成分と樹脂に耐熱性を付与する成分とから構成される耐熱性樹脂と、露光により酸を発生する下記一般式［I］で示される感光性化合物と、この両者を溶解可能な溶剤とを含んで成ることを特徴とするレジスト材料。

$$R^6-O_2S-\underset{\underset{N_2}{\|}}{C}-SO_2-R^7 \qquad [\text{I}]$$

［式中、R6、R7は夫々独立して炭素数1～10の直鎖状，分枝状又は環状のアルキル基、炭素数1～10のハロアルキル基、炭素数2～10のアルケニル基、フェニル基、置換フェニル基（置換基は、ハロゲン原子、炭素数1～10の直鎖状，分枝状又は環状のアルキル基、炭素数1～10の直鎖状又は分枝状のアルコキシ基、炭素数1～10のハロアルキル基、ニトロ基、ニトリル基又はアミド基）、アラルキル基又は置換アラルキル基（置換基は、ハロゲン原子、炭素数1～10の直鎖状，分枝状又は環状のアルキル基、炭素数1～10の直鎖状又は分枝状のアルコキシ基、炭素数1～10のハロアルキル基、ニトロ基、ニトリル基又はアミド基）を表わす。］

(2)酸雰囲気下で加熱により化学変化を受けてアルカリ可溶性となる官能基を有する成分と樹脂に耐熱性を付与する成分とから構成される耐熱性樹脂が下記一般式［II］

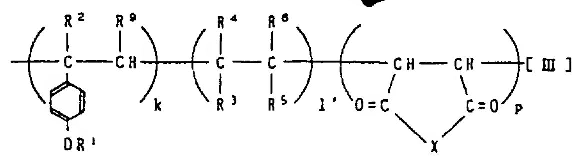


［II］

［式中、R1はメチル基、イソプロピル基、tert-ブチル基、メトキシメチル基、イソプロポキシメチル基、テトラヒドロピラニル基、テトラヒドロフラニル基、トリメチルシリル基、tert-ブトキシカルボニル基又はイソプロポキシカルボニル基

を表わし、R^2は水素原子、ハロゲン原子又はメチル基を表わし、R^3は水素原子、p-ヒドロキシフェニル基、p-クロルフェニル基、フェニル基、シアノ基又は-$COOR^7$（但し、R^7は炭素数3～10の分岐状又は環状のアルキル基、又は水素原子を表わす。）を表わし、R^4及びR^6は夫々独立して水素原子、メチル基又はハロゲン原子を表わし、R^5は水素原子、シアノ基又は-$COOR^8$（但し、R^8は炭素数3～10の分岐状又は環状のアルキル基、又は水素原子を表わす。）を表わし、R^9は水素原子又は-$COOR^{10}$（但し、R^{10}は炭素数3～10の分岐状又は環状のアルキル基、又は水素原子を表わす。）を表わし、k及びlは夫々独立して自然数を表わす。］で示される樹脂である請求項(1)に記載のレジスト材料。

(3)酸雰囲気下で加熱により化学変化を受けてアルカリ可溶性となる官能基を有する成分と樹脂に耐熱性を付与する成分とから構成される耐熱性樹脂が下記一般式［Ⅲ］



［式中、Xは酸素原子又は N-$(CH_2)_q$-R^{11}（但し、R^{11}は炭素数1～10の直鎖状、分岐状又は環状のアルキル基又は置換基を有していても良いフェニル基を表わし、qは0又は自然数を表わす。）を表わし、l'及びpは夫々独立して0又は自然数を表わし、R^1, R^2, R^3, R^4, R^5, R^6, R^9及びkは前記と同じ。］で示される樹脂である請求項(1)に記載のレジスト材料。

3. 発明の詳細な説明

［産業上の利用分野］

本発明は半導体素子等の製造に於て用いられるレジスト材料に関する。詳しくは露光エネルギー源として400nm以下の光源、例えば365nmのｉ線光、300nm以下の遠紫外光、例えば248.4nmのKrFエキシマレーザー光等を用いてポジ型のパターンを形成する際のレジスト材料に関する。

［従来の技術］

近年、半導体デバイスの高密度集積化に伴い、微細加工、中でもフォトリソグラフィに用いられる露光装置の光源は益々、短波長化し、今ではKrFエキシマレーザ（248.4nm）光が検討されるまでになってきている。しかしながらこの波長に適したレジスト材料は未だ適当なものが見出されていない。

例えば、KrFエキシマレーザ光に対してかなり感光性が高く、光透過率も良いと言われているＭＰ2400（シプレイ社製）を用いた場合、ベースポリマーのノボラック樹脂自身の露光光に対する大きな表面吸収や感光剤のナフトキノンジアジド系化合物の光反応性が良くない為、現像後のパターン形状は非常に悪く使用出来ない。また、KrFエキシマレーザ光や遠紫外光を光源とするレジスト材料として248.4nm付近の光に対する透過性が高い樹脂と分子内に $\overset{O}{\overset{\|}{-C}}-\overset{N_2}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$ 基を有する感光性化合物より成るレジスト材料が開発されている。（例えば、特開昭64-80944号公報；特開平1-154048号公報；特開平1-155339号公報等）。

さらに分子内に $\overset{O}{\overset{\|}{-C}}-\overset{N_2}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$ 基と-SO_2Cl基を有する感光性化合物と248.4nm付近で高い光透過性を有する樹脂より成るパターン形成材料も開発されている。（例えば、特開平1-188852号公報；Y.Taniら、SPIE's 1989 Sympo.,1086-03等）。第４図を用いて、このレジスト材料によるパターン形成方法を示す。半導体基板１上にレジスト材料５を回転塗布し、1.0μmのレジスト材料膜を得る（第４図(ａ)）。なお、基板１上には酸化膜、導電膜、絶縁膜が形成されている場合が多い。次に248.4nmのKrFエキシマレーザ光３でマスク４を介し選択的に露光する（第４図(ｂ)）。そして最後に通常のアルカリ現像液（0.24％テトラメチルアンモニウムヒドロキシド水溶液）を用いて現像を行うことによりレジスト材料５の露光部を溶解除去しパターン５ａを得る（第４図(ｃ)）。このレジスト材料膜（1μm）の露光前後の紫外線分光曲線を第５図に示す。使用樹脂が1μm厚で70％であるのに対し、このレジスト材料の露光後の透過率は40

%と低く、十分な光褪色性が得られていないことがわかる。また、パターン形成実験の結果、パターンのアスペクト比は約70度と十分なパターン形状は得られていない。更にこのレジスト材料膜（1μm）のγ特性を第6図に示すが、このレジスト材料の感度は約140～150mJ/cm²であった。$-\overset{O}{\overset{\|}{C}}-\overset{N_2}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$基を有する感光性化合物を含むレジスト材料を使用する場合、一般的にその感度は100～300mJ/cm²程度であり、高出力の割にエネルギー効率が良くないKrFエキシマレーザ光（248.4nm）を用いての実用化は困難な状況にある。また、近年、露光エネルギー量を低減させる手段として露光により発生した酸を媒体とする化学増幅型のレジスト材料が提案され［H.Itoら、Polym.Eng.Sci.,23巻,1012頁(1983年)］、これに関して種々の報告がなされている。（例えば、W.R.Brunsvoldら,SPIE's 1989 Sympo.,1086-40；T.Neenanら,SPIE's 1989 Sympo.,1086-01）。しかしながら、これ等化学増幅型レジスト材料に使用される樹脂は比較的、芳香環を多く有することに起因して248.4nm付近の光透過性が不十分であったり、樹脂の耐熱性が乏しい等の問題がある。

また、感光性化合物に関しては、例えばトリフェニルスルホニウムテトラフルオロボレイトのようなオニウム塩の場合は溶液安定性が乏しくレジスト材料を調製した直後ではその本来の性能を発揮するが半導体製造ラインに於て実用化することは困難であると言われているし、2,6-ジニトロベンジルのスルホン酸エステルの場合は化合物としての安定性は認められるが露光により生成する2-ニトロ-6-ニトロソベンズアルデヒドが一般に使われている現像液（テトラメチルアンモニウムヒドロキシド水溶液）に溶解しないため、現像処理後、露光部にスカムが残存したり、パターン形状が悪くなる等の問題が生ずる。また、トリス（メタンスルホニルオキシ）ベンゼンは前記感光性化合物と比べて感度が低いため化学増幅型レジストの感光性化合物としては適さない。

［発明が解決しようとする問題点］

このように$-\overset{O}{\overset{\|}{C}}-\overset{N_2}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$基を有する感光性化合物を含むレジスト材料の場合には、感光性化合物の光褪色性が悪いことと$-\overset{O}{\overset{\|}{C}}-\overset{N_2}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$基を光反応させなければならないことから、良好なパターン形状が得られ難く、且つ露光エネルギー量を多く必要とする。また、化学増幅型レジスト材料については樹脂の248.4nm付近の光透過性を改善するか、樹脂の耐熱性を向上させない限り使用に供し得ないし、また同時に感光性化合物に関してはより低い露光エネルギー量で酸を発生し、且つ溶液安定性があり、しかも光反応により発生した酸が高い透過性を有することが求められている。

［発明の目的］

本発明は上記した如き状況に鑑みなされたもので、i線光や、遠紫外光、例えばKrFエキシマレーザ光等による露光後に高い透過性を有し、且つ耐熱性を有する樹脂と、高感度（低露光エネルギー量）で効率良く酸を発生し、且つ溶液中で安定で、しかも光反応により発生した酸が高い透過性を有する感光性化合物を含んで成るレジスト材料を提供することを目的とする。

［発明の構成］

上記目的を達成するため、本発明は下記の構成より成る。

「酸雰囲気下で加熱により化学変化を受けてアルカリ可溶性となる官能基を有する成分と樹脂に耐熱性を付与する成分とから構成される耐熱性樹脂と、露光により酸を発生する下記一般式［I］で示される感光性化合物と、この両者を溶解可能な溶剤とを含んで成ることを特徴とするレジスト材料。

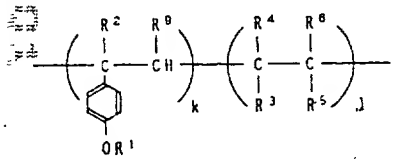
$$R_0^1-O_2S-\underset{\underset{N_2}{\|}}{C}-SO_2-R_0^2 \qquad [I]$$

［式中、R_0^1、R_0^2は夫々独立して炭素数1～10の直鎖状，分枝状又は環状のアルキル基、炭素数1～10のハロアルキル基、炭素数2～10のアルケニル基、フェニル基、置換フェニル基（置換基は、ハロゲン原子、炭素数1～10の直鎖状，分枝状又は環状のアルキル基、炭素数1～10の直鎖状又は分枝状のアルコキシ基、炭素数1～10のハロアルキル基、ニトロ基、ニトリル基又はアミド基）、ア

ラルキル基又は置換アラルキル基（置換基は、ハロゲン原子、炭素数1～10の直鎖状，分枝状又は環状のアルキル基、炭素数1～10の直鎖状又は分枝状のアルコキシ基、炭素数1～10のハロアルキル基、ニトロ基、ニトリル基又はアミド基）を表わす。］」

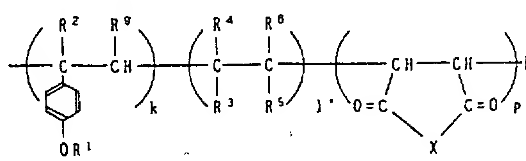
本発明のレジスト材料は露光エネルギー量を出来るだけ低減させるため、化学増幅を利用したものである。即ち、本発明のレジスト材料は露光により酸発生剤から発生した酸の雰囲気下、加熱により化学変化を受けてアルカリ可溶性となる官能基を有する成分と、樹脂に耐熱性を付与する成分即ち加熱に対し樹脂全体が軟化することを抑止する機能を有する成分とから構成される耐熱性樹脂（以下、「本発明に係る樹脂」と略記する。）と新規な感光性化合物とを併せ用いる点に特徴を有する新規なレジスト材料である。本発明に係る酸雰囲気下、加熱によりアルカリ可溶性となる官能基を有する成分（以下、「特定の官能基を有する成分」と略記する。）としては例えば酸で脱離する保護基を有するp-ヒドロキシスチレン誘導体やp-ヒドロキシ-α-メチルスチレン誘導体等のモノマーが挙げられる。具体例としては例えばp-メトキシスチレン、p-イソプロポキシスチレン、p-tert-ブトキシスチレン、p-メトキシメトキシスチレン、p-イソプロポキシメトキシスチレン、p-テトラヒドロピラニルオキシスチレン、p-テトラヒドロフラニルオキシスチレン、p-トリメチルシリルオキシスチレン、p-tert-ブトキシカルボニルオキシスチレン、p-イソプロポキシカルボニルオキシスチレン、或はこれ等p-ヒドロキシスチレン誘導体と同様の保護基を有するp-ヒドロキシ-α-メチルスチレン誘導体等が挙げられるが、勿論これらに限定されるものではない。また、樹脂に耐熱性を付与する成分としてはこの成分の使用により樹脂全体が100℃以上の加熱、より好ましくは140℃以上の加熱でも軟化することを抑止出来るものであればいずれにても良いが、例えばp-ヒドロキシスチレン、p-クロルスチレン、スチレン、α-メチルスチレン、フマロニトリル、マレイン酸モノイソプロピル、マレイン酸モノtert-ブチル、マレイン酸ジtert-ブチル、マレイン酸モノシクロヘキシル、無水マレイン酸、N-フェニルマレイミド、N-置換フェニルマレイミド、N-メチルマレイミド、N-n-ブチルマレイミド等のモノマーがより一般的なものとして挙げられる。

本発明に係る樹脂は例えば下記一般式［Ⅱ］又は［Ⅲ］であらわすことが出来る。



［Ⅱ］

［式中，R^1はメチル基、イソプロピル基、tert-ブチル基、メトキシメチル基、イソプロポキシメチル基、テトラヒドロピラニル基、テトラヒドロフラニル基、トリメチルシリル基、tert-ブトキシカルボニル基又はイソプロポキシカルボニル基を表わし、R^2は水素原子、ハロゲン原子又はメチル基を表わし、R^3は水素原子、p-ヒドロキシフェニル基、p-クロルフェニル基、フェニル基、シアノ基又は-$COOR^7$（但し、R^7は炭素数3～10の分岐状又は環状のアルキル基、又は水素原子を表わす。）を表わし、R^4及びR^6は夫々独立して水素原子、メチル基又はハロゲン原子を表わし、R^5は水素原子、シアノ基又は-$COOR^8$（但し、R^8は炭素数3～10の分岐状又は環状のアルキル基、又は水素原子を表わす。）を表わし、R^9は水素原子又は-$COOR^{10}$（但し、R^{10}は炭素数3～10の分岐状又は環状のアルキル基、又は水素原子を表わす。）を表わし、k及びlは夫々独立して自然数を表わす。］



［Ⅲ］

［式中、Xは酸素原子又は $N\text{-}(CH_2)q\text{-}R^{11}$（但し、$R^{11}$は炭素数1～10の直鎖状、分岐状又は環状のアルキル基又は置換基を有していても良いフェニル基を表わし、qは0又は自然数を表わす。）を表わし、l'及びpは夫々独立して0又は自然数を表わし、R^1，R^2，R^3，R^4，R^5，R^6，R^9及びkは前記と

同じ。]

これら一般式[Ⅱ]又は[Ⅲ]で表わされる化合物は、本発明に係る樹脂の代表的なものであるが、本発明に係る樹脂は勿論これらの化合物に限定されるものではない。

本発明に係る樹脂の具体例としては例えば、p-イソプロポキシスチレンとα-メチルスチレン共重合体、p-テトラヒドロピラニルオキシスチレンとp-ヒドロキシスチレン共重合体、p-tert-ブトキシスチレンとp-ヒドロキシスチレン共重合体、p-tert-ブトキシカルボニルオキシスチレンとマレイン酸モノシクロヘキシルエステル共重合体、p-tert-ブトキシカルボニルオキシスチレンとα-メチルスチレン共重合体、p-tert-ブトキシスチレンとフマロニトリル共重合体、p-メトキシメトキシスチレンとp-クロルスチレン共重合体、p-メトキシメトキシスチレンとマレイン酸モノシクロヘキシルエステル及び無水マレイン酸との共重合体、p-テトラヒドロフラニルオキシスチレンとN-メチルマレイミド共重合体、p-tert-ブトキシカルボニルオキシスチレンとp-ヒドロキシスチレン及び無水マレイン酸との共重合体、p-テトラヒドロピラニルオキシスチレンとp-ヒドロキシスチレン及びフマロニトリルとの共重合体、p-tert-ブトキシカルボニルオキシスチレンとp-ヒドロキシスチレン及びN-ブチルマレイミドとの共重合体、p-テトラヒドロピラニルオキシスチレンとp-ヒドロキシスチレン及びN-フェニルマレイミドとの共重合体等が挙げられるが、これ等に限定されるものではない。

本発明に係る樹脂は、上記特定の官能基を有する成分(モノマー)1種又は2種以上と樹脂に耐熱性を付与する成分(モノマー)1種又は2種以上とを共重合体製造法の常法に従って共重合させることにより容易に得ることができる。即ち、上記特定の官能基を有する成分(モノマー)1種又は2種以上と樹脂に耐熱性を付与する成分(モノマー)1種又は2種以上とを例えばベンゼン、トルエン等の有機溶媒中、ラジカル重合開始剤[例えばアゾビスイソブチロニトリル、2,2'-アゾビス(2,4-ジメチルワレロニトリル)、2,2'-アゾビス(2-メチルプロピオン酸メチル)等のアゾ系重合開始剤や過酸化ベンゾイル、過酸化ラウロイル等の過酸化物系重合開始剤等]の存在下、窒素気流中50～100℃で1～10時間重合反応させればよく、反応後は高分子化合物取得法の常法に従って後処理を行ないこれを単離すればよい。

本発明に係る樹脂は、また、市販のポリ(p-ビニルフェノール)のような重合体に前記特定の官能基を化学反応により適宜導入する方法によっても容易に得ることができることは言うまでもない。

本発明に係る樹脂の重量平均分子量($\overline{Mw}$)は通常1,000～40,000程度、好ましくは3,000～20,000程度である。

本発明で用いられる一般式[Ⅰ]で示される感光性化合物に於て、R_6', R_6''で示される直鎖状，分枝状又は環状のアルキル基のアルキル基及びハロアルキル基のアルキル基としては、例えばメチル基，エチル基，プロピル基，ブチル基，アミル基，ヘキシル基，オクチル基，デシル基等炭素数1～10のアルキル基が挙げられ、ハロアルキル基のハロゲンとしては、塩素，臭素，弗素，沃素が挙げられ、アルケニル基としては、例えばビニル基，1-プロペニル基，2-プロペニル基(アリル基)，2-ブテニル基，イソプロペニル基，1,3-ブタジエニル基，2-ペンテニル基，1-ヘキセニル基等炭素数2～10のアルケニル基が挙げられ、アラルキル基としては、例えばベンジル基，フェネチル基，フェニルプロピル基，フェニルブチル基等炭素数7～10のアラルキル基が挙げられる。また、置換フェニル基及び置換アラルキル基の置換基である直鎖状，分枝状又は環状のアルキル基のアルキル基、直鎖状又は分枝状のアルコキシ基のアルキル基及びハロアルキル基のアルキル基としては、例えばメチル基，エチル基，プロピル基，ブチル基，アミル基，ヘキシル基，オクチル基，デシル基等炭素数1～10のアルキル基が挙げられ、ハロゲン原子及びハロアルキル基のハロゲンとしては塩素，臭素，弗素，沃素が挙げられる。

本発明者らは露光により酸を発生する感光性化

合物について鋭意研究の途上、露光によりブリーチする感光性化合物、即ち上記一般式〔I〕で示される感光性化合物を用いた場合には、その内部セル効果により、従来の感光性化合物を用いた場合よりも露光後の透過性が著しく改善され、解像度が大幅に向上することを見出し、本発明を完成するに至つた。

本発明で用いられる溶剤としては、樹脂と感光性化合物の両者を溶解可能なものであれば何れにても良いが、通常は365nm及び248.4nm付近に吸収を有しないものがより好ましく用いられる。より具体的にはエチルセロソルブアセテート、メチルセロソルブアセテート、ジエチレングリコールジメチルエーテル、乳酸エチル、乳酸メチル、ジオキサン又はエチレングリコールモノイソプロピルエーテル等が挙げられるが勿論これ等に限定されるものではない。

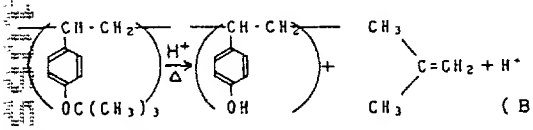
本発明に係る樹脂は300nm以上の波長領域で光の吸収がなく、365nmのｉ線光には極めて高い光透過性を有している。また、酸発生剤についてもｉ線光でも酸が発生する事が確認されており、化学増幅作用が利用出来る。従って、本発明のレジスト材料は化学増幅方法を利用して低露光量のKrFエキシマレーザ光（248.4nm）やｉ線光（365nm）を用いてパターン形成可能なレジスト材料である。

〔作用〕

本発明の作用について説明すると、先ず、KrFエキシマレーザ光、ｉ線光等で露光された部位は例えば下記（A）で示される光反応に従って酸が発生する。

$$R_6\text{-}O_2S\text{-}\underset{\underset{N_2}{\|}}{C}\text{-}SO_2\text{-}R_6 \xrightarrow{h\nu} \left[R_6\text{-}O_2S\text{-}\underset{\underset{R_6}{|}}{C}{=}SO_2\right] \xrightarrow{H_2O} R_6\text{-}O_2S\text{-}\underset{\underset{R_6}{|}}{C}HSO_3H \qquad (A)$$

露光工程に続いて加熱処理すると下記（B）の反応式に従って樹脂の官能基が酸により化学変化を受け、アルカリ可溶性となり、現像の際、現像液に溶出してくる。



（B）

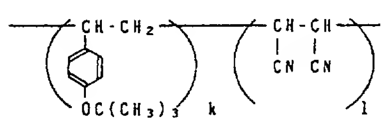
他方、未露光部は酸が発生しない為、加熱処理しても化学変化は起らず、アルカリ可溶性基の発現はない。また、樹脂自身の耐熱性が高い為、加熱処理時、樹脂の軟化は認められない。このように本発明のレジスト材料を用いてパターン形成を行った場合には露光部と未露光部との間でアルカリ現像液に対して大きな溶解度差を生じ、しかも、未露光部の樹脂が加熱処理時、軟化しないのでその結果、良好なコントラストを有したポジ型のパターンが形成される。また、前記反応式（B）で示されるように露光で発生した酸は触媒的に作用する為、露光は必要な酸を発生させるだけでよく、露光エネルギー量の低減が可能となる。

〔実施例〕

以下に実施例、参考例を挙げて本発明を更に詳細に説明するが、本発明はこれ等により何ら制約を受けるものではない。

参考例　1.

p-tert-ブトキシスチレン88g及びフマロニトリル39gを2,2'-アゾビス(2-メチルプロピオン酸メチル)の存在下、トルエン溶媒中、窒素気流下、90℃で2時間重合反応させた。反応後、反応液をメタノール中に注入して晶析させ、析出晶を濾取、乾燥してp-tert-ブトキシスチレン-フマロニトリル共重合体（$\overline{Mw}$ 約10,000）



(k/l=1/1)

120gを得た。

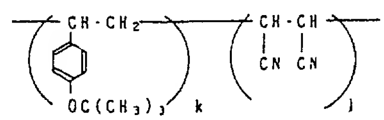
実施例　1.

下記の組成から成るレジスト材料を調製した。

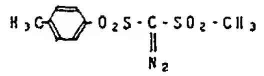
p-tert-ブトキシスチレン-

フマロニトリル共重合体

（参考例1で得られた化合物）



(k/l=1/1)　6.0g

 0.5g

ジエチレングリコールジメチルエーテル 15.0g

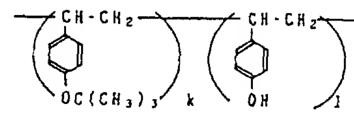
第1図を用いて上記レジスト材料を使用したパターン形成方法を説明する。半導体等の基板1上に上記レジスト材料2を回転塗布し、90℃、90秒間ホットプレートでソフトベーク後、1.0μmの膜厚のレジスト材料膜を得た（第1図(a)）。次に248.4nmのKrFエキシマレーザ光3をマスク4を介して選択的に露光した（第1図(b)）。そして130℃、90秒間ホットプレートでベーク後、アルカリ現像液（2.38%テトラメチルアンモニウムヒドロキシド水溶液）で60秒間現像することにより、レジスト材料2の露光部のみを溶解除去し、ポジ型パターン2aを得た（第1図(c)）。このレジスト材料膜（1μm）の露光前後の紫外線分光曲線を第2図に示す。露光前は約55%の透過率が、露光後は約78%と高い透過性を示している。また、この時のポジ型パターンのアスペクト比は約88度の好形状の0.25μmラインアンドスペースパターンであった。更にこのレジスト材料膜（1μm）のγ特性を第3図に示す。この材料は最小露光量約18mJ/cm²という高感度であった。

実施例　2．

実施例1に於て樹脂を下記に示すスチレン系樹脂に変更し、それ以外は実施例1と同様にしてレジスト材料を調製し、実施例1と同様の実験を行った。

p-tert-ブトキシスチレン-

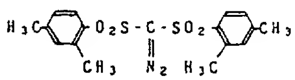
p-ヒドロキシスチレン共重合体($\overline{Mw}$ 約13,000)

 (k/l=1/1)

その結果、実施例1と同様の良好な結果が得られた。このレジスト材料を用いて得たポジ型パターンは約15mJ/cm²の露光エネルギー量でパターン形成が可能であった。

実施例　3．

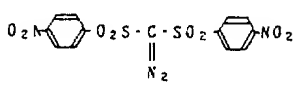
実施例1に於て感光性化合物を下記に示す化合物に変更し、それ以外は実施例1と同様にしてレジスト材料を調製し、実施例1と同様の実験を行った。



その結果、実施例1と同様の良好な結果が得られた。このレジスト材料を用いて得たポジ型パターンは約23mJ/cm²の露光エネルギー量でパターン形成が可能であった。

実施例　4．

実施例2に於て感光性化合物を下記に示す化合物に変更し、それ以外は実施例2と同様にしてレジスト材料を調製し、実施例2と同様の実験を行った。

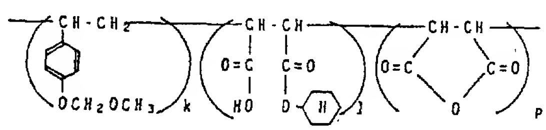


その結果、実施例2と同様の良好な結果が得られた。このレジスト材料を用いて得たポジ型パターンは約32mJ/cm²の露光エネルギー量でパターン形成が可能であった。

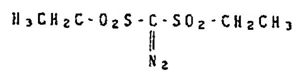
実施例　5．

p-メトキシメトキシスチレン-

マレイン酸系共重合体（$\overline{Mw}$ 約15,000）



(k/l/p=2/1/1)　6.0g

 0.3g

ジエチレングリコールジメチルエーテル 15.0g

上記の組成で調製されたレジスト材料を用いて実施例1と同様の実験を行った。

その結果、実施例1と同様の良好な結果が得られた。このレジスト材料を用いて得たポジ型パターンは約15mJ/cm²の露光エネルギー量でパターン形成が可能であった。

［発明の効果］

本発明に係るレジスト材料を400nm以下の光源例えば365nmのi線光、300nm以下の遠紫外光（Deep UV）、例えばKrFエキシマレーザ光（248.4nm）等の露光用レジスト材料として用いた場合

には、サブミクロンオーダーの形状の良い微細なパターンが容易に得られる。従って本発明は、半導体産業等に於ける超微細パターンの形成にとって大きな価値を有するものである。

尚、本レジスト材料はｉ線光や遠紫外光、KrFエキシマレーザ光で特に効果を発揮するが、電子線やＸ線でも充分使用が可能である。

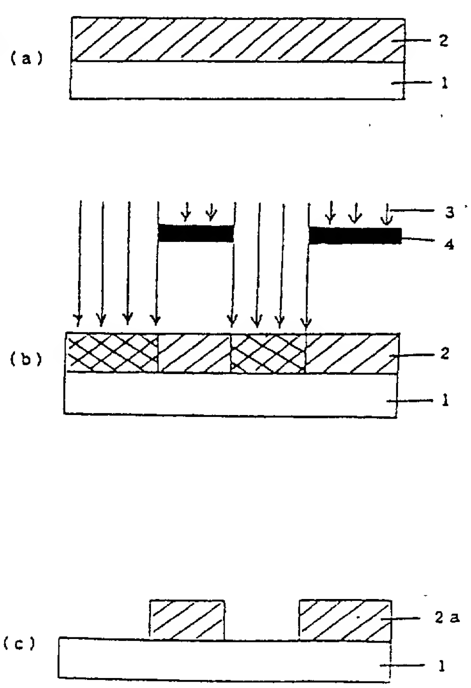
4．図面の簡単な説明

第１図～第３図は実施例１で得られた結果を示し、第１図は本発明のレジスト材料を用いたパターン形成方法の工程断面図、第２図は本発明のレジスト材料の紫外線分光曲線図（但し、実線は露光前、破線は露光後）、第３図は本発明のレジスト材料のγ特性図を夫々示す。また第４図は従来のレジスト材料を用いたパターン形成方法の工程断面図、第５図は従来のレジスト材料の紫外線分光曲線図（但し、実線は露光前、破線は露光後）、第６図は従来のレジスト材料のγ特性図である。

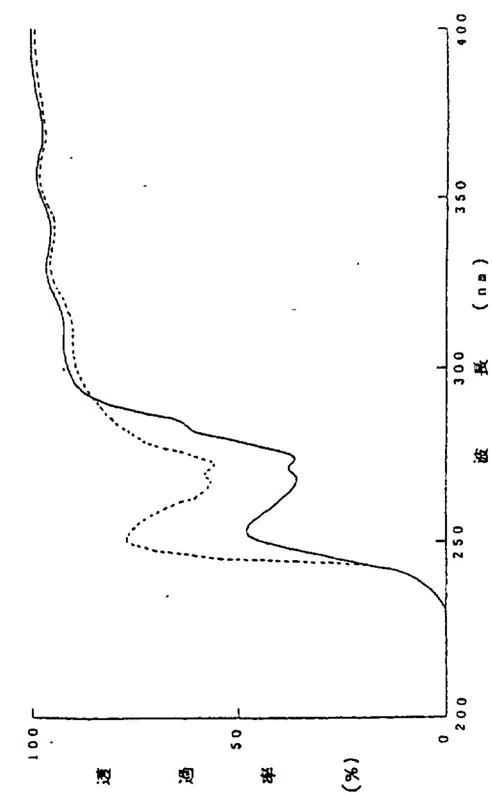
１…基板、２…本発明のレジスト材料膜、３…KrFエキシマレーザ光、４…マスク、５…従来のレジスト材料膜、２a…樹脂パターン。

特許出願人　和光純薬工業株式会社

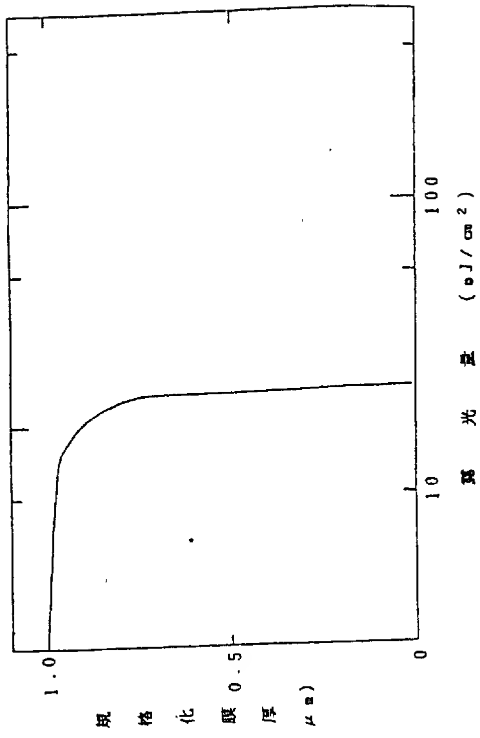
第　１　図



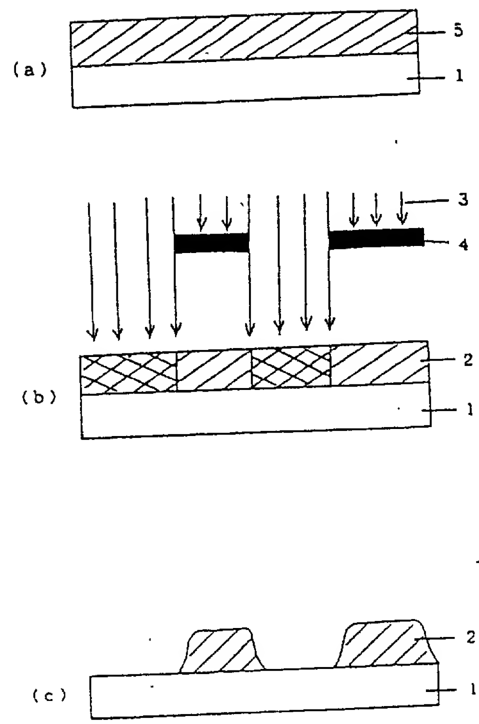
第　２　図



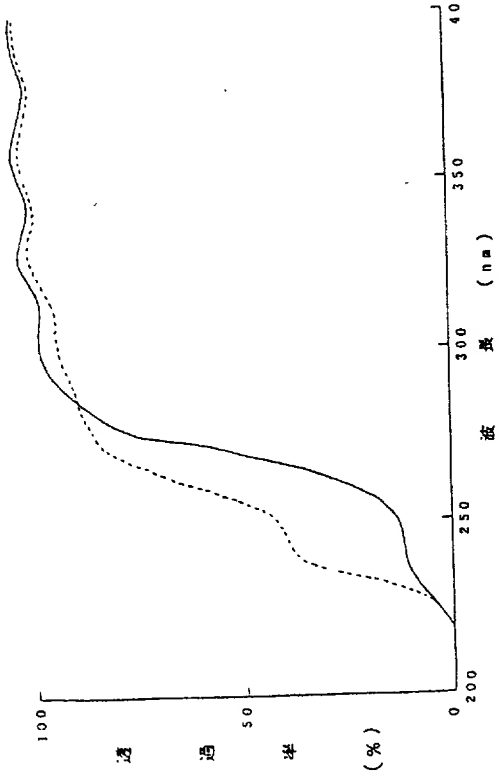
第3図



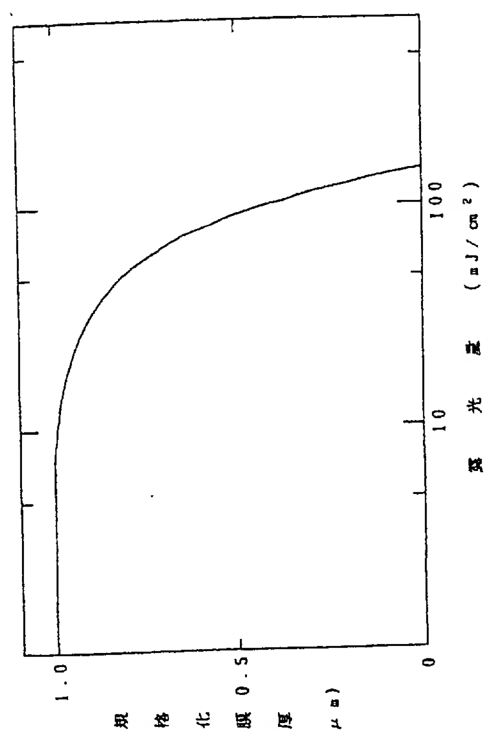
第4図



第5図



第6図



Translation of JP Kokai 3-223863

(Appln. No. 2-19614, filed Jan. 30, 1990)

S P E C I F I C A T I O N

1. Title of the invention

A resist material

2. The claims

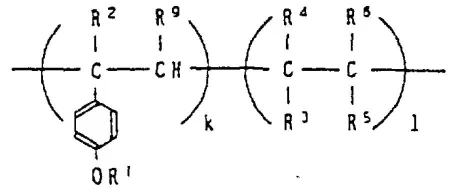
(1) A resist material characterized by comprising a heat-resistant resin consisting of a constituent having functional groups capable of being imparted with alkali solubility by undergoing a chemical change by heating under an atmosphere of acid and a constituent capable of imparting heat resistance to the resin, a photosensitive compound capable of generating an acid by exposure to light as represented by the general formula [I] given below and a solvent capable of dissolving both of them:

$$R^1_0-O_2S-\underset{\underset{N_2}{\|}}{C}-SO_2-R^2_0 \qquad [I]$$

[in the formula, R^1_0 and R^2_0 denote, each independently from the other, a straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms, haloalkyl group having 1 to 10 carbon atoms, alkenyl group having 2 to 10 carbon atoms, phenyl group, substituted phenyl group (the substituent group being a halogen atom, straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms, straightly linear or branched alkoxy group having 1 to 10 carbon atoms, haloalkyl group having 1 to 10 carbon atoms, nitro group, nitrile group or amido group), aralkyl group or substituted aralkyl group (the substituent group being a halogen atom, straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms, straightly linear or branched alkoxy group having 1 to 10 carbon atoms, haloalkyl group having 1 to 10 carbon atoms, nitro group, nitrile group or amido group)].

(2) The resist material described in Claim 1 in which the heat-resistant resin consisting of a constituent having functional groups capable of being imparted with alkali solubility

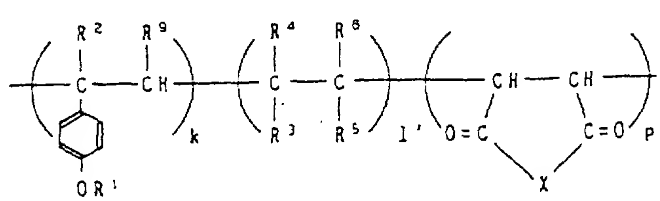
by undergoing a chemical change by heating under an atmosphere of acid and a constituent capable of imparting heat resistance to the resin is a resin represented by the general formula [II] given below:



[II]

[in the formula, R^1 denotes a methyl group, isopropyl group, tert-butyl group, methoxymethyl group, isopropoxymethyl group, tetrahydropyranyl group, tetrahydrofuranyl group, trimethylsilyl group, tert-butoxycarbonyl group or isopropoxycarbonyl group, R^2 denotes a hydrogen atom, halogen atom or methyl group, R^3 denotes a hydrogen atom, p-hydroxyphenyl group, p-chlorophenyl group, phenyl group, cyano group or $-COOR^7$ (R^7 denoting a branched or cyclic alkyl group having 3 to 10 carbon atoms or hydrogen atom), R^4 and R^6 denote, each independently from the other, a hydrogen atom, methyl group or halogen atom, R^5 denotes a hydrogen atom, cyano group or $-COOR^8$ (R^8 denoting a branched or cyclic alkyl group having 3 to 10 carbon atoms or hydrogen atom), R^9 denotes a hydrogen atom or $-COOR^{10}$ (R^{10} denoting a branched or cyclic alkyl group having 3 to 10 carbon atom or hydrogen atom) and k and l denote, each independently from the other, a natural number].

(3) The resist material described in Claim 1 in which the heat-resistant resin consisting of a constituent having functional groups capable of being imparted with alkali solubility by undergoing a chemical change by heating under an atmosphere of acid and a constituent capable of imparting heat resistance to the resin is a resin represented by the general formula [III] given below:



[III]

[in the formula, X is an oxygen atom or N-$(CH_2)_q$-R^{11} (R^{11} denoting a straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms or phenyl group optionally having a substituent group and q denotes 0 or a natural number), l' and p denote, each independently from the other, 0 or a natural number and R^1, R^2, R^3, R^4, R^5, R^6, R^9 and k each have the same meaning as above].

3. Detailed description of the invention

[Field of industrial application]

The present invention relates to a resist material used in the manufacture of semiconductor devices and the like. More particularly, related to is a resist material for the formation of a positive pattern by the use of a light source of 400 nm or shorter such as the i-line light of 365 nm, far ultraviolet light of 300 nm or shorter such as the KrF excimer laser beam of 248.4 nm and the like, as the energy source of light exposure.

[Prior art technology]

Along with the trend toward higher densities of integration in semiconductor devices, in recent years, the light source of light exposure apparatuses used in fine works or, inter alia, photolithography is shifting toward shorter wavelengths now resulting in the study of KrF excimer laser beams (248.4 nm). Nevertheless, none has been discovered yet of the resist materials suitable for this wavelength.

When MP 2400 (a product by Shipley Co.), accepted to have a considerably high photosensitivity and good light transmissivity to the KrF excimer laser beams, is used, for example, it is not suitable for use due to the very poor pattern profile after development as a consequence of the large surface absorption of the novolac resin per se as the base polymer to the exposure light and the low photoreactivity of the naphthoquinone diazide-based compound as the photosensitizing agent. Further, a resist material comprising a resin having high transmissivity to the light in the vicinity of 248.4 nm and a photosensitive compound having a -CO-CN_2-CO- group in the molecule has been developed as a resist material for the KrF excimer laser beams or far ultraviolet light as the light source (for example,

official publication of Japanese Patent Kokai No. 64-80944, official publication of Japanese Patent Kokai No. 1-154048, official publication of Japanese Patent Kokai No. 1-155339 and elsewhere).

Also, there has been developed a pattern-forming material comprising a photosensitive compound having a $-CO-CN_2-CO-$ group and a $-SO_2Cl$ group in the molecule (for example, official publication of Japanese Patent Kokai No. 1-188852, Y. Tani, et al., SPIE's 1989 Sympo., 1086-03 and elsewhere). By making reference to Figure 4, a method for pattern formation is illustrated with this resist material. A semiconductor substrate 1 is spin-coated with the resist material 5 to give a resist material film of 1.0 μm (Figure 4(a)). Incidentally, it is often the case here that an oxidized film, electroconductive film and insulating film are formed on the substrate 1. In the next place, selective light exposure is undertaken through a mask 4 with a KrF·excimer laser beam 3 of 248.4 nm (Figure 4(b)). In the last place, thereafter, the resist material 5 in the exposed areas is dissolved and removed away by performing development using a conventional alkaline developer solution (0.24% aqueous solution of tetramethylammonium hydroxide) to give a pattern 5a (Figure 4(c)). Figure 5 shows the ultraviolet spectra of this resist material film (1 μm) before and after the light exposure. As compared with 70% in the resin used in a thickness of 1 μm, this resist material after exposure to light exhibits a low transmittance of 40% to indicate that no sufficient photofading can be obtained. As a result of a pattern forming experiment, besides, the aspect ratio of the pattern is about 70 degrees not to give a satisfactory pattern profile. Further, Figure 6 shows the γ-characteristic of this resist material film (1 μm), according to which the sensitivity of this resist material is about 140 to 150 mJ/cm^2. In the use of a resist material containing a photosensitive compound having a $-CO-CN_2-CO-$ group, the sensitivity is, usually, around 100 to 300 mJ/cm^2 so that it is the present status that a difficulty is encountered in the practical application by the use of the KrF excimer laser beam (248.4 nm) having a low energy efficiency

notwithstanding the high output. In recent years, furthermore, a chemical-sensitization resist material utilizing an acid generated by light exposure as an intermedium is proposed as a means for decreasing the energy dose of light exposure [H. Ito, et al., Polym. Eng. Sci., volume 23, page 1012 (1983)] and various reports have been submitted relating thereto (for example, W.R. Brunsvold, et al., SPIE's 1989 Sympo., 1086-40 and T. Neenan, et al., SPIE's 1989 Sympo., 1086-01). The resins used in these chemical-sensitization resist materials, however, have problems of low light transmissivity in the vicinity of 248.4 nm as a consequence of a relatively large number of aromatic rings therein, poor heat resistance of the resin and so on.

Further, as to the photosensitive compound, for example, onium salts such as triphenyl sulfonium tetrafluoroborate are said to have a difficulty in the practical application in a semiconductor manufacturing line due to the low stability of solution, although their inherent performance can be exhibited immediately after preparation of the resist material, and esters of 2,6-dinitrobenzyl sulfonic acid, although stability of the compound as such can be acknowledged, are subject to occurrence of problems of scums left on the exposed areas, poor pattern profile and so on after a development treatment because 2-nitro-6-nitroso benzaldehyde formed by light exposure is insoluble in the developer solution conventionally under use (aqueous solution of tetramethylammonium hydroxide). Further, tris-(methane sulfonyloxy) benzene is not suitable as a photosensitive compound in a chemical-sensitization resist due to the low sensitivity as compared with the above mentioned photosensitive compounds.

[Problems to be solved by the invention]

Thus, it is unavoidable for a resist material containing a photosensitive compound having a $-CO-CN_2-CO-$ group that a good pattern profile can hardly be obtained and a large exposure energy dose is required because the photofading of the photosensitive compound is low and the $-CO-CN_2-CO-$ groups must be brought under a photoreaction. Further, chemical-sensitization

resist materials cannot be used unless the light transmissivity of the resin in the vicinity of 248.4 nm is improved or the heat resistance of the resin is increased and, in the same time, the photosensitive compound is required to generate an acid with a decreased light exposure energy dose and to have stability as a solution along with a high transmissivity of the acid generated by the photoreaction.

[Object of the invention]

The present invention, which has been completed in view of the above described situations, has an object to provide a resist material comprising a resin having high transmissivity after light exposure with the i-line light, far ultraviolet light such as KrF excimer laser beams and the like and a photosensitive compound capable of efficiently generating an acid with high sensitivity (low light exposure energy dose) and exhibiting stability in a solution along with high transmissivity of the acid generated by the photoreaction.

[Constitution of the invention]

The constitution of the present invention is as follows to accomplish the above described object.

"A resist material characterized by comprising a heat-resistant resin consisting of a constituent having functional groups capable of being imparted with alkali solubility by undergoing a chemical change by heating under an atmosphere of acid and a constituent capable of imparting heat resistance to the resin, a photosensitive compound capable of generating an acid by exposure to light as represented by the general formula [I] given below and a solvent capable of dissolving both of them:

$$R^1_0\text{-}O_2S\text{-}\underset{\underset{N_2}{\|}}{C}\text{-}SO_2\text{-}R^2_0 \qquad [I]$$

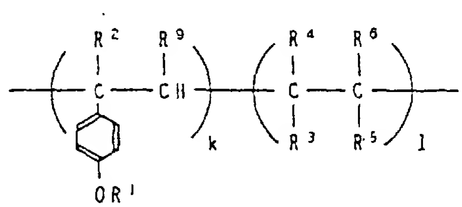
[in the formula, R^1_0 and R^2_0 denote, each independently from the other, a straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms, haloalkyl group having 1 to 10 carbon atoms, alkenyl group having 2 to 10 carbon atoms, phenyl group, substituted phenyl group (the substituent group being

a halogen atom, straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms, straightly linear or branched alkoxy group having 1 to 10 carbon atoms, haloalkyl group having 1 to 10 carbon atoms, nitro group, nitrile group or amido group), aralkyl group or substituted aralkyl group (the substituent group being a halogen atom, straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms, straightly linear or branched alkoxy group having 1 to 10 carbon atoms, haloalkyl group having 1 to 10 carbon atoms, nitro group, nitrile group or amido group)]."

Chemical sensitization is utilized in the resist material of the present invention in order to minimize the light exposure energy dose. Namely, the resist material of the present invention is a novel resist material characterized by using, in combination, a heat-resistant resin (referred to as "the resin according to the present invention" hereinafter) consisting of a constituent having a functional group capable of being rendered alkali-soluble by undergoing a chemical change by heating under an atmosphere of the acid generated from an acid generating agent by exposure to light and a constituent capable of imparting heat resistance to the resin or, namely, a constituent having an activity to suppress softening of the resin as a whole against heating and a novel photosensitive compound. The constituent having a functional group capable of being rendered alkali soluble by heating under an atmosphere of acid according to the present invention (referred to as "the constituent having a specified functional group" hereinafter) is exemplified, for example, by the monomers having a protective group dissociable with an acid such as p-hydroxystyrene derivatives, p-hydroxy-α -methyl styrene derivatives and the like. Particular examples include, for example, p-methoxy styrene, p-isopropoxy styrene, p-tert-butoxy styrene, p-methoxymethoxy styrene, p-isopropoxymethoxy styrene, p-tetrahydropyranyloxy styrene, p-tetrahydrofuranyloxy styrene, p-trimethylsilyloxy styrene, p-tert-butoxycarbonyloxy styrene and p-isopropoxycarbonyloxy styrene as well as p-hydroxy-α -methylstyrene derivatives having similar protective groups to those in these

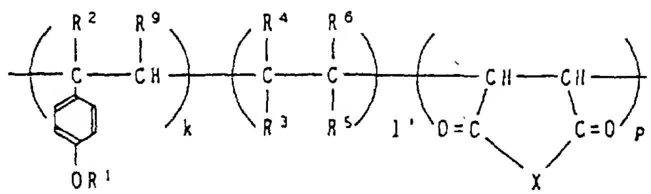
p-hydroxystyrene derivatives and so on, though not limited thereto as a matter of course. Further, the constituent capable of imparting heat resistance to the resin, which can be any one provided that softening of the resin as a whole even by heating at 100 ℃ or higher or, more preferably, by heating at 140 ℃ or higher can be suppressed by the use of this constituent, is exemplified, for example, by the monomers such as p-hydroxystyrene, p-chlorostyrene, styrene, α-methylstyrene, fumaronitrile, monoisopropyl maleate, mono-tert-butyl maleate, di-tert-butyl maleate, monocyclohexyl maleate, maleic anhydride, N-phenyl maleimide, N-substituted phenyl maleimides, N-methyl maleimide, N-n-butyl maleimide and the like as more generally suitable ones.

The resin according to the present invention can be expressed, for example, by the general formula [II] or [III] given below.



[II]

[in the formula, R^1 denotes a methyl group, isopropyl group, tert-butyl group, methoxymethyl group, isopropoxymethyl group, tetrahydropyranyl group, tetrahydrofuranyl group, trimethylsilyl group, tert-butoxycarbonyl group or isopropoxycarbonyl group, R^2 denotes a hydrogen atom, halogen atom or methyl group, R^3 denotes a hydrogen atom, p-hydroxyphenyl group, p-chlorophenyl group, phenyl group, cyano group or $-COOR^7$ (R^7 denoting a branched or cyclic alkyl group having 3 to 10 carbon atoms or hydrogen atom), R^4 and R^6 denote, each independently from the other, a hydrogen atom, methyl group or halogen atom, R^5 denotes a hydrogen atom, cyano group or $-COOR^8$ (R^8 denoting a branched or cyclic alkyl group having 3 to 10 carbon atoms or hydrogen atom), R^9 denotes a hydrogen atom or $-COOR^{10}$ (R^{10} denoting a branched or cyclic alkyl group having 3 to 10 carbon atoms or hydrogen atom) and k and l denote, each independently from the other, a natural number]

 [III]

[in the formula, X is an oxygen atom or $N-(CH_2)_q-R^{11}$ (R^{11} denoting a straightly linear, branched or cyclic alkyl group having 1 to 10 carbon atoms or phenyl group optionally having a substituent group and q denotes 0 or a natural number), l' and p denote, each independently from the other, 0 or a natural number and R^1, R^2, R^3, R^4, R^5, R^6, R^9 and k each have the same meaning as above]

Although these resins represented by the general formula [II] or [III] are typical ones of the resin according to the present invention, the resin according to the present invention is never limited to these compounds as a matter of course.

Particular examples of the resin according to the present invention include, for example, copolymers of p-isopropoxy styrene and α-methylstyrene, copolymers of p-tetrahydropyranyloxy styrene and p-hydroxystyrene, copolymers of p-tert-butoxy styrene and p-hydroxystyrene, copolymers of p-tert-butoxycarbonyloxy styrene and monocyclohexyl ester of maleic acid, copolymers of p-tert-butoxycarbonyloxy styrene and α-methylstyrene, copolymers of p-tert-butoxy styrene and fumaronitrile, copolymers of p-methoxymethoxy styrene and p-chlorostyrene, copolymers of p-methoxymethoxy styrene, monocyclohexyl ester of maleic acid and maleic anhydride, copolymers of p-tetrahydrofuranyloxy styrene and N-methyl maleimide, copolymers of p-tert-butoxycarbonyloxy styrene, p-hydroxystyrene and maleic anhydride, copolymers of p-tetrahydropyranyloxy styrene, p-hydroxystyrene and fumaronitrile, copolymers of p-tert-butoxycarbonyloxy styrene, p-hydroxystyrene and N-butyl maleimide, copolymers of p-tetrahydropyranyloxy styrene, p-hydroxystyrene and N-phenyl maleimide and the like, though not limitative thereto.

The resin according to the present invention can be easily obtained by conducting copolymerization of one kind or two kinds

or more of the above described constituents (monomers) having a specified functional group and one kind or two kinds or more of the constituents (monomers) capable of imparting heat resistance to the resin according to the conventional method for the preparation method of copolymers. Namely, for example, one kind or two kinds or more of the above described constituents (monomers) having a specified functional group and one kind or two kinds or more of the constituents (monomers) capable of imparting heat resistance to the resin are subjected to a polymerization reaction for 1 to 10 hours at 50 to 100 ℃ under a stream of nitrogen in an organic solvent such as benzene, toluene and the like in the presence of a radical polymerization initiator [for example, an azo-based polymerization initiator such as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethyl valeronitrile), 2,2'-azobis(methyl 2-methylpropionate) and the like, peroxide-based polymerization initiator such as benzoyl peroxide, lauroyl peroxide and the like, and so on] and the reaction is followed by a post-treatment according to a conventional method for obtaining a polymeric compound to isolate the same.

It may be needless to say, furthermore, that the resin according to the present invention can be easily obtained by a method in which the above mentioned specific functional group is adequately introduced into a polymer such as a commercially available poly(p-vinylphenol) by a chemical reaction.

The resin according to the present invention has a weight-average molecular weight ($\overline{Mw}$) of, usually, around 1000 to 40,000 or, preferably, around 3000 to 20,000.

In the photosensitive compound represented by the general formula [I] to be used in the present invention, the alkyl group of the straightly linear, branched or cyclic alkyl groups denoted by R^1。 and R^2。 and the alkyl group of the haloalkyl groups are exemplified, for example, by the alkyl groups having 1 to 10 carbon atoms such as methyl group, ethyl group, propyl group, butyl group, amyl group, hexyl group, octyl group, decyl group and the like, the halogen of the haloalkyl group is exemplified by chlorine, bromine, fluorine and iodine, the

alkenyl group is exemplified, for example, by the alkenyl groups of 2 to 10 carbon atoms such as vinyl group, 1-propenyl group, 2-propenyl group (allyl group), 2-butenyl group, isopropenyl group, 1,3-butadienyl group, 2-pentenyl group, 1-hexenyl group and the like and the aralkyl group is exemplified, for example, by the aralkyl groups of 7 to 10 carbon atoms such as benzyl group, phenethyl group, phenylpropyl group, phenylbutyl group and the like. Further, the alkyl group of the straightly linear, branched or cyclic alkyl groups as the substituent group of the substituted phenyl groups and substituted aralkyl groups, the alkyl group of the straightly linear or branched alkoxy groups and the alkyl group of the haloalkyl groups are exemplified, for example, by the alkyl groups of 1 to 10 carbon atoms such as methyl group, ethyl group, propyl group, butyl group, amyl group, hexyl group, octyl group, decyl group and the like and the halogen of the haloalkyl groups is exemplified by chlorine, bromine, fluorine and iodine.

On the way of extensive investigations for a photosensitive compound capable of generating an acid by exposure to light, the inventors have discovered that the transmissivity after exposure to light is greatly improved and the image resolution is greatly increased when a photosensitive compound susceptible to bleaching by light exposure or, namely, the photosensitive compound represented by the above given general formula [I] is used by virtue of the internal cell effect as compared with the use of a conventional photosensitive compound leading to completion of the present invention.

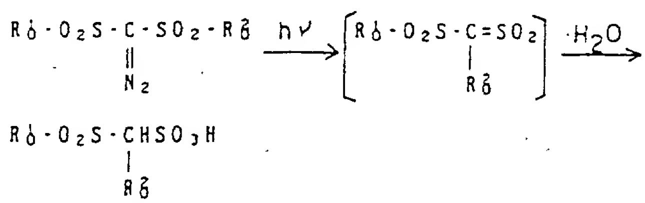
As the solvent used in the present invention, which can be any of those capable of dissolving both of the resin and the photosensitive compound, usually those having no absorption in the vicinity of 365 nm and 248.4 nm are used more preferably. More particularly, it is exemplified by ethyl Cellosolve acetate, methyl Cellosolve acetate, diethyleneglycol dimethyl ether, ethyl lactate, methyl lactate and dioxane as well as ethyleneglycol monoisopropyl ether and the like, though not limitative thereto as a matter of course.

The resin according to the present invention has no light

absorption in the wavelength region of 300 nm or longer and has very high light transmissivity to the i-line light of 365 nm. Further, generation of an acid with the i-line light has been confirmed from the acid generating agent enabling utilization of the chemical sensitization effect. Accordingly, the resist material of the present invention is a resist material with which pattern formation is possible using the KrF excimer laser beam (248.4 nm) or i-line light (365 nm) of a low light exposure dose by the utilization of the method of chemical sensitization.

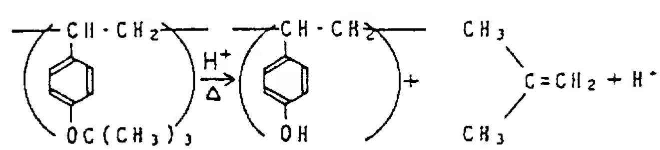
[Performance]

To give a description on the performance of the present invention, firstly, an acid is generated in the portion exposed to the KrF excimer laser beams, i-line light and the like, for example, according to the photoreaction shown by (A) given below.



(A)

When the step of light exposure is followed by a heat treatment, a chemical change takes place on the functional groups of the resin by the acid according to the reaction equation (B) given below to be rendered alkali-soluble so as to be dissolved away in the developer solution by development.



(B)

On the other hand, no chemical changes take place in the unexposed areas by a heat treatment not to cause appearance of alkali-soluble groups because no acid is generated there. Since the resin per se has high heat resistance, furthermore, softening of the resin is not found in the course of the heat treatment. When pattern formation is thus undertaken by using the resist material of the present invention, a great difference

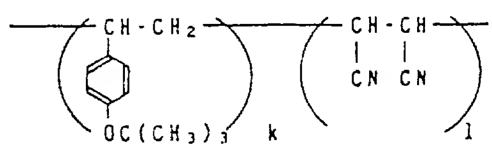
is produced in the solubility in an alkaline developer solution between the exposed areas and unexposed areas and, in addition, the resin in the unexposed areas does not cause softening in the course of the heat treatment so that, as a consequence thereof, a positive pattern having good contrast is formed. Further, as is shown by the above given reaction equation (B), the acid generated by exposure to light has a catalytic activity so that the exposure to light can be so low as only to generate a requisite acid enabling to decrease the exposure light energy dose.

[Examples]

In the following, the present invention is described in more detail by way of Examples and Reference Examples which, however, never limit the present invention in any way.

Reference Example 1.

A polymerization reaction of 88 g of p-tert-butoxy styrene and 39 g of fumaronitrile was conducted in toluene as a solvent at 90 ℃ for 2 hours under a stream of nitrogen in the presence of 2,2'-azobis(methyl 2-methylpropionate). After the reaction, the reaction mixture was poured into methanol to cause precipitation of crystals and the precipitated crystals were collected by filtration and dried to give 120 g of a copolymer of p-tert-butoxy styrene and fumaronitrile ($\overline{Mw}$ about 10,000).

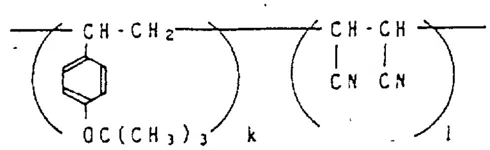


(k/l=1/1)

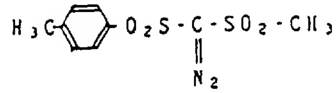
Example 1.

A resist material consisting of the following composition was prepared.

Copolymer of p-tert-butoxy styrene and fumaronitrile (compound obtained in Reference Example 1)



(k/l=1/1) 6.0 g



0.5 g

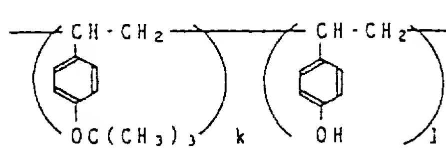
Diethyleneglycol dimethyl ether 15.0 g

The method for pattern formation using the above described resist material is illustrated by using Figure 1. A substrate 1 such as a semiconductor and the like was spin-coated with the above described resist material 2 which was subjected to soft-baking on a hot plate at 90 ℃ for 90 seconds to give a resist material film of 1.0 μm film thickness (Figure 1(a)). In the next place, selective exposure was performed through a mask 4 with the KrF excimer laser beams 3 of 248.4 nm (Figure 1(b)). Then, baking on a hot plate for 90 seconds at 130 ℃ was followed by development for 60 seconds with an alkaline developer solution (2.38% aqueous solution of tetramethylammonium hydroxide) so that the resist material 2 in the exposed areas only was dissolved and removed away to give a positive pattern 2a (Figure 1(c)). Figure 2 shows the ultraviolet spectra of this resist material film (1 μm) before and after exposure to light. While the transmittance is about 55% before exposure, a high transmittance of about 78% is exhibited after exposure. Further, the positive pattern here was a line-and-space pattern of 0.25 μm having a good profile with an aspect ratio of about 88 degrees. Figure 3 further shows the γ-characteristic of this resist material film (1 μm). This material had a high sensitivity with a minimum exposure dose of about 18 mJ/cm^2.

Example 2.

A resist material was prepared in the same manner as in Example 1 excepting for the replacement of the resin in Example 1 with a styrene-based resin shown below and the same experiment as in Example 1 was undertaken.

Copolymer of p-tert-butoxy styrene and p-hydroxystyrene ($\overline{Mw}$ about 13,000)

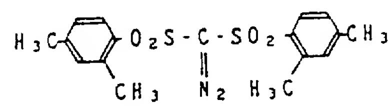


(k/l=1/1)

As a result, the same satisfactory results as in Example 1 could be obtained. Pattern formation of a positive pattern obtained by using this resist material was possible with a light exposure energy dose of about 15 mJ/cm^2.

Example 3.

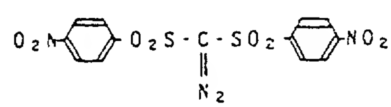
A resist material was prepared in the same manner as in Example 1 excepting for the replacement of the photosensitive compound in Example 1 with a compound shown below and the same experiment as in Example 1 was undertaken.



As a result, the same satisfactory results as in Example 1 could be obtained. Pattern formation of a positive pattern obtained by using this resist material was possible with a light exposure energy dose of about 23 mJ/cm^2.

Example 4.

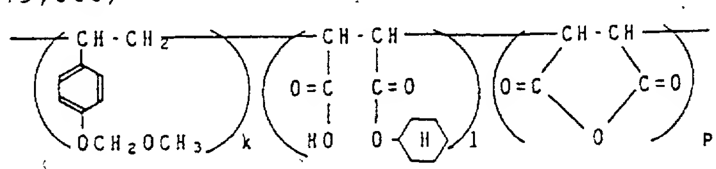
A resist material was prepared in the same manner as in Example 2 excepting for the replacement of the photosensitive compound in Example 2 with a compound shown below and the same experiment as in Example 2 was undertaken.



As a result, the same satisfactory results as in Example 2 could be obtained. Pattern formation of a positive pattern obtained by using this resist material was possible with a light exposure energy dose of about 32 mJ/cm^2.

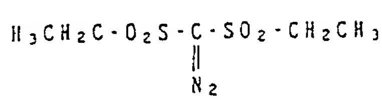
Example 5.

Copolymer of p-methoxymethoxy styrene and maleic acid ($\overline{Mw}$ about 15,000)



6.0 g

(k/l/p=2/1/1)



0.3 g

Diethyleneglycol dimethyl ether 15.0 g

The same experiment as in Example 1 was undertaken by using a resist material prepared in the above described composition.

As a result, the same satisfactory results as in Example 1 could be obtained. Pattern formation of a positive pattern obtained by using this resist material was possible with a light exposure energy dose of about 15 mJ/cm^2.

[Advantages of the invention]

When the resist material according to the present invention is used as a resist material for exposure to light with a light of 400 nm or shorter such as the i-line light of 365 nm, far ultraviolet light of 300 nm or shorter (deep UV) such as the KrF excimer laser beams (248.4 nm) and the like, a fine pattern of the submicron order having a good profile can easily be obtained. Accordingly, the present invention has a great value for the formation of an ultrafine pattern in the semiconductor industry and the like.

Incidentally, this resist material can be used quite satisfactorily with electron beams and X-rays although advantageous effects can be exhibited particularly with the i-line light, far ultraviolet light and KrF excimer laser beams.

4. Brief description of the drawing

Figure 1 to Figure 3 each show the results obtained in Example 1, of which Figure 1 is a cross sectional figure of the process steps in the method of pattern formation by the use of the resist material of the present invention, Figure 2 shows the ultraviolet spectra of the resist material of the present invention (in which the solid line is for that before light exposure and the broken line is for that after light exposure) and Figure 3 shows a graph of the γ-characteristic of the resist material of the present invention. And, Figure 4 is a cross sectional figure of the process steps in the method of pattern formation by the use of a conventional resist material, Figure 5 shows the ultraviolet spectra of a conventional resist material (in which the solid line is for that before light exposure and the broken line is for that after light exposure) and Figure 6 shows a graph of the γ-characteristic of a

conventional resist material.

1···substrate, 2···film of the resist material of the present invention, 3···KrF excimer laser beam, 4···mask, 5···film of conventional resist material, 2a···resin pattern

Applicant for patent: Wako Pure Chemical Industries, Ltd.

FIGURE 1

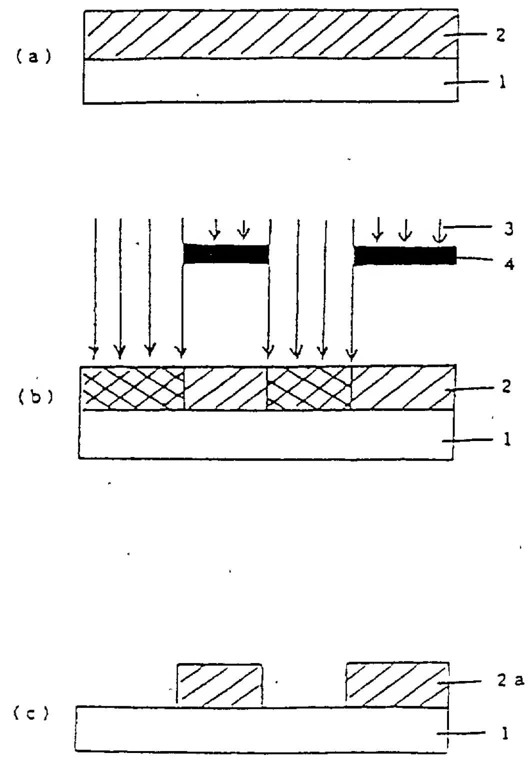


FIGURE 2

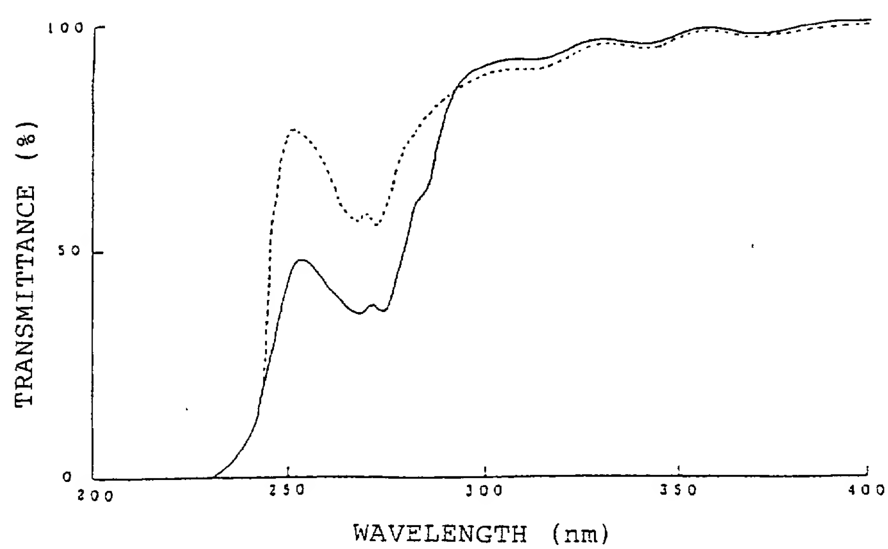


FIGURE 3

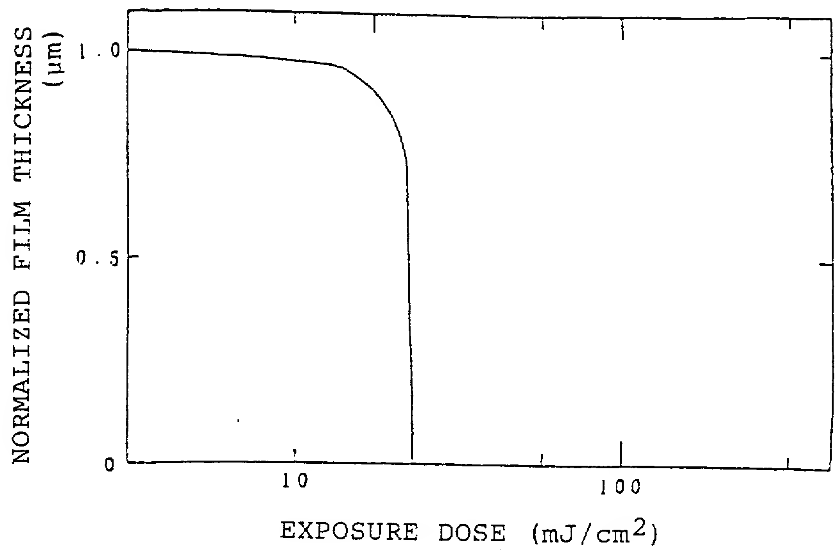


FIGURE 4

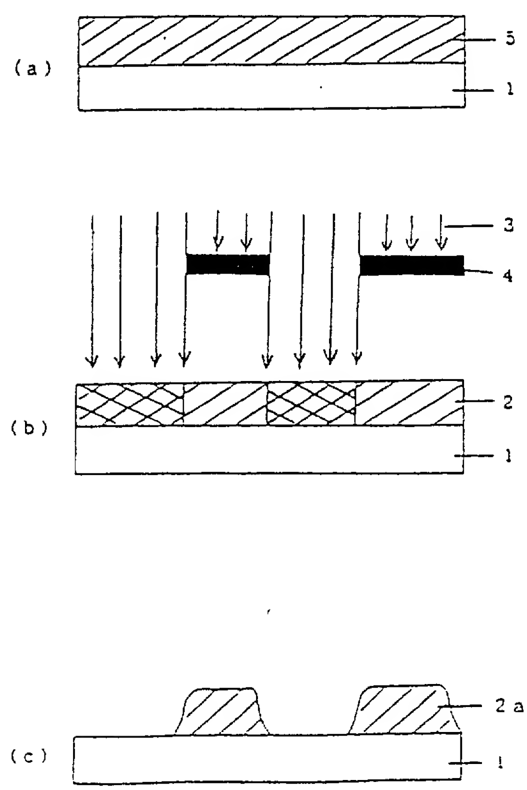


FIGURE 5

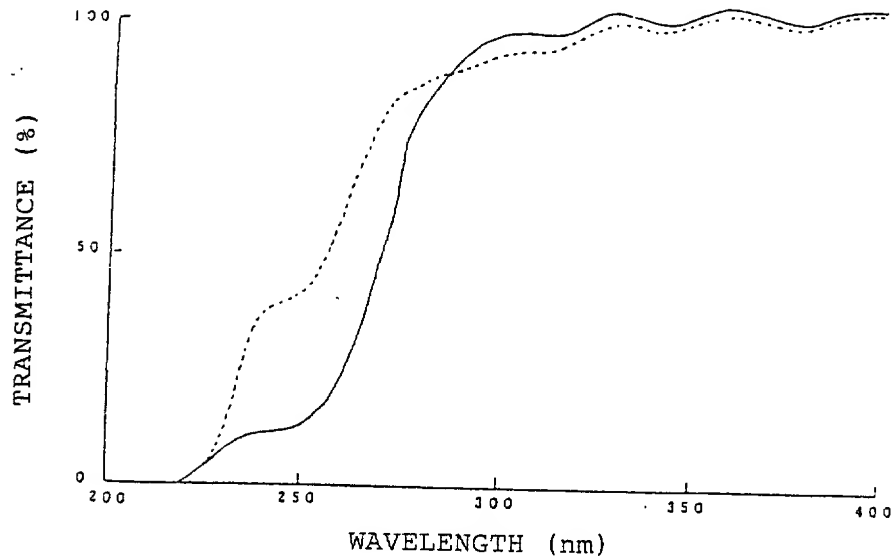


FIGURE 6